

2000 Annual Report

RESEARCH AND REFERENCE ACTIVITIES

**Laboratory Services Branch
Ontario Ministry of the Environment
March, 2001**

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2000 Annual Report
Research and Reference Activities
Laboratory Services Branch
March 2001

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Overview

The title of this report has been changed in recognition of the growing importance of LSB analytical reference services to the Ministry and to the Ontario laboratory community. From assistance to individual Ontario private laboratories to collaborations with technology development companies in the evaluation of new instruments, the range of Reference Centre activities has never been greater. Included in these activities are participation in international round-robin studies, and the development of environmental real-matrix certified reference materials.

More smaller-scale R&D projects were active this past year – ones that required a less concentrated effort and shorter time-frame to complete. This means that a larger part of the R&D effort was directed towards specific new methods requested by LSB customers, rather than longer-term technology development initiatives. The specific analytes investigated ranged from volatile organic compounds (VOCs) in air and formaldehyde in drinking water to toxaphene congeners, the mixed chlorinated/brominated dioxins/furans, and metals in road dust. As usual, a full range of environmental sample types including air, water, soil, and biota were investigated.

For further information on any of the projects or activities described in this report, readers are directed to the Study Leader, or to the Author:

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A. New Applications of Technology

Introduction

Most of the technology development work in 2000 involved various mass spectrometry techniques. The use of GC-MS, LC-MS and ICP-MS were all investigated as the best technologies to solve various complex analytical challenges. A relatively new mass spectrometry technique called Time-of-Flight (TOFMS) was examined for the first time by LSB staff, in collaboration with an instrument manufacturing company. TOFMS has been around for decades, but recent improvements in computers, electronics, and manufacturing techniques have finally led to the production of TOF instruments that seem ideal for high throughput environmental applications. It is too soon to say whether TOFMS will become a dominant technology for environmental applications, but it seems clear that the importance of mass spectrometry technologies for environmental analysis will continue to grow for the foreseeable future.

One of the non-MS based technologies that has made a big impact in recent years is Accelerated Solvent Extraction (ASE), which is also called Pressurized Fluid Extraction. This technology has shown great promise for the rapid and efficient extraction of trace organics from a wide variety of environmental sample types. LSB staff have just started to evaluate this technology, with promising results. The initial LSB studies of ASE are reported within.

I. LC-MS/MS Methods for Nonylphenol and Nonylphenol Ethoxylates

Study Leaders:	Patrick Crozier and Vince Taguchi [Mass Spectrometry Section]
Collaborators:	J. Plomley, Y. Mouget and T. Hoffman [MDS Sciex]
Customer:	I. Smith [Water Policy Branch]; R. Kettry [Canada Ontario Agreement]; M. Marsh [Standards Development Branch]; J. Chan [Metro Toronto Works]

Objectives

To develop selective and sensitive mass spectrometry methods for the quantitative determination of nonylphenol (NP) and nonylphenol ethoxylates (NPEOs) in a variety of sample types; to use LC-MS/MS methods for confirming the presence and concentration of NP and NPEOs in sewage treatment plant (STP) wastewater and pelletized sludge.

Background

NPEOs are non-ionic surfactants used in domestic and industrial cleaners as well as in the textile and pulp and paper industries. Because they are a component of various cleaners, NPEOs have been detected in various wastewater streams including STPs. NPEOs are of environmental concern because of their tendency to degrade to NP. NP and the lower molecular weight NPEO congeners are members of a group of chemicals known as *endocrine disruptors* – thought to cause growth and reproductive problems in biota. Health Canada has designated NP and NPEOs as toxic under the Canadian Environmental Protection Act (CEPA). NP and NPEOs are also included in sewage discharge and land drainage regulations for the City of Toronto (By-Law 457-2000, July 2000). NP and NPEOs concentrations in discharge waters are not to exceed 1 ug/L and 10ug/L, respectively. Despite the concern with regard to NP and NPEOs, very few rugged, selective and sensitive analytical techniques exist for their detection in complex matrices such as STP influents, effluents and sludges. LSB is approaching the environmental monitoring of NP and NPEOs by developing a rapid flow injection (FIA)-MS/MS screening technique that would give a presence/absence of total NP and

NPEOs above/below a specified guideline. Presence above the guideline would result in further speciation of NP and NPEOs by quantitative LC-MS/MS. This approach would eliminate the need for speciation of samples when NP and NPEOs are present below the specified guideline.

LSB has previously reported a rapid screening technique for NPEOs detection in STPs using precursor ion scanning coupled to flow injection analysis. The FIA-MS/MS method provides a NPEO homologue groups profile for sample comparisons along with a semi-quantitative analytical result. To complement this screening procedure, LSB is developing a method involving normal phase chromatographic separation of NPEO homologue groups coupled to APCI with tandem mass spectrometric detection. To enhance the quantitative aspects of the method, pure standards of individual homologue groups were produced from technical mixtures by preparative chromatography using HPLC/APCI/MS data-dependent fraction collection techniques.

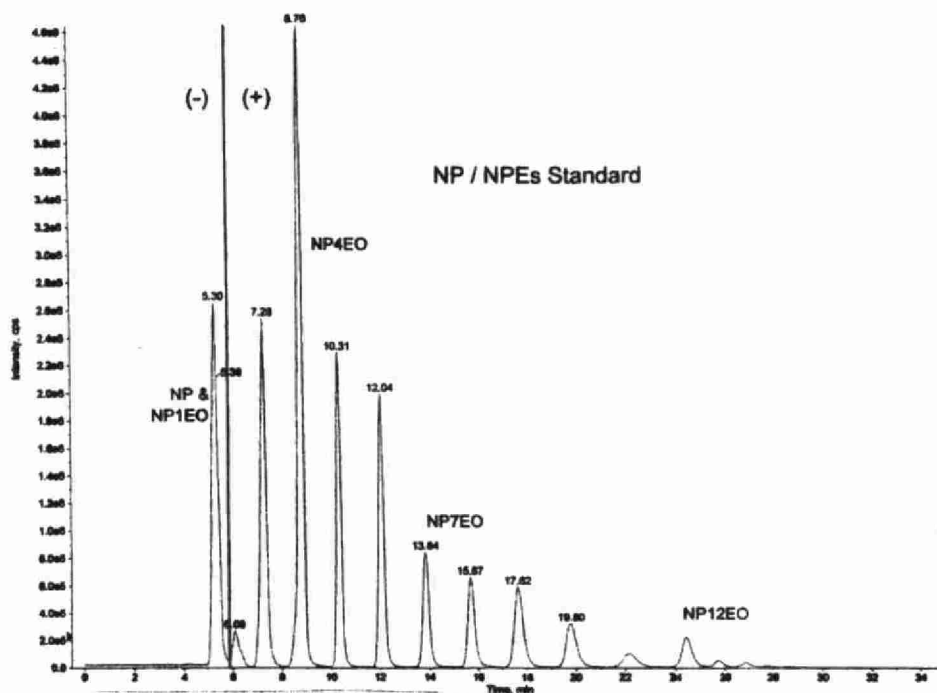
Results

Very few sources of pure NP and NPEOs exist, especially for the heavier ethoxylate homologues. Pure standards containing linear alkyl side chains are available but these are not found in the environment because manufacturers use technical mixtures containing branched alkyl side-chains for cost reasons. Technical grade standards (Igepal™ or Surfonic™) having branched alkyl side-chains are readily available but are comprised of a conglomeration of congeners/isomers. Preparative separation of NPEO homologue groups from Surfonic™ technical blends (Huntsman Corporation) was done using ammoniated silica stationary supports (Phenomenex Hypersil 5um NH₂) with a normal phase gradient elution. The preparative column flow was split post-column to a single quadrupole mass spectrometer and a fraction collector. The fraction collector was triggered to collect individual solvent fractions by the mass spectrometer when a user specified APCI/SIM response threshold for a specific ionic species (i.e. [M+H]⁺), characteristic of the homologue group, was exceeded. Pure standards of the individual NPEO homologue groups were produced.

The basic skeleton of a quantitative normal phase LC-(API) MS/MS analytical method has been developed. Some work must still be done in order to complete the method. STP samples (influent, effluent and primary/secondary sludge) were acidified

and extracted with dichloromethane. The extracts were then dried with sodium sulphate, reduced to dryness, reconstituted in methanol and spiked with $^{13}\text{C}_6$ -NP and $^{13}\text{C}_6$ -NP3EO. Final extracts were analysed using an MDS Sciex API3000TM LC-triple quadrupole mass spectrometer. NP and NPEOs were separated at a flow rate of 1.0 mL/min on a heated (28°C) 250 mm x 4.6 mm Phenomenex Hypersil NH₂ column using a binary gradient consisting of hexane/isopropyl alcohol (IPA) and IPA/water. The chromatographic eluent was ionized under APCI conditions. Tandem MS collision energies were optimized for the most abundant MRM transition for NP and each NPEO. All components were baseline resolved and eluted in under 30 minutes (see figure). Mass spectrometric detection was segmented into two periods coinciding to the elution of NP/ $^{13}\text{C}_6$ -NP and NPE2O-NP16EO. In the first period, NP and $^{13}\text{C}_6$ -NP internal standard were analyzed in negative ion mode for the MRM transitions m/z 219→133 and m/z 225→112, respectively. After elution of NP/ $^{13}\text{C}_6$ -NP, the MS polarity was switched to positive ion mode in the second period for the detection of NP2EO-NP16EO. The response of the polyethoxylates was related to the internal standard $^{13}\text{C}_6$ -NP3EO. Quadrupoles Q1 and Q3 were operated at unit resolution (0.7 Da FWHM). Operating the quadrupoles at unit resolution was essential for minimizing the transmission of matrix interferences. Five point calibration curves were constructed for each homologue group with correlation coefficients > 0.998. Instrumental detection limits (IDL) as low as 3 pg/μL were achievable with signal-to-noise ratios >3:1.

Using the calculated response factor from the $^{13}\text{C}_6$ -NP and $^{13}\text{C}_6$ -NP3EO internal standards, it was possible to characterize the adulteration in the NP/NPEOs content between STP influent and effluent, such that removal efficiency and homologue redistribution could be ascertained. There are two notable deficiencies with the method at present; 1) poor chromatographic separation and ionization of NP1EO, and 2) interferences in the NP7EO and NP8EO MRM transitions in some STP samples. Elimination of NP7EO and NP8EO interferences may be done by selecting other MRM transitions or by some form of sample cleanup prior to instrumental analysis. The NP1EO issue is much more complex and requires further study of both chromatographic and ionization conditions. The NP1EO issue *must* be resolved because NP1EO exhibits the most estrogenic activity of the NPEO homologues, second only to NP itself.



Current Status

Access to the MDS Sciex API3000™ LC-triple quadrupole mass spectrometer used for the work was severely limited in 2000. LSB acquired a new LC-triple quadrupole instrument at the end of March, 2001. Fine tuning of the normal phase LC-MS/MS analytical method, to include the nonylphenol monoethoxylate and reduce interferences in a couple of NPEO homologue group MRM transitions, will be done when the new instrument is delivered and operational.

Publications and Presentations

P. W. Crozier, J. B. Plomley and V. Y. Taguchi. The Characterization of Nonylphenol Ethoxylates in Sewage Treatment Plants Using Liquid Chromatography - Tandem Mass Spectrometry. Proceedings of the Third Biennial International Conference on Chemical Measurement and Monitoring of the Environment (EnviroAnalysis 2000), Ottawa, Ontario, Canada, May 8 - 11, 2000.

T. Hoffman, Y. Mouget, J. Plomley, P. Crozier and V. Taguchi. Normal Phase HPLC/APCI/MS Data-Dependent Fraction Collection of Preparatively Separated Homologues of Nonylphenol Polyethoxylates. The 48th ASMS Conference on Mass Spectrometry and Allied Topics, Long Beach, California, USA, June 11 - 15, 2000.

II. HPLC/ES/Isotope Dilution-MS Analysis of Glyphosate and Aminomethyl Phosphonic Acid in Water and Vegetation Samples

Study Leader:	L. Grey [Applied Chromatography Section]
Study Team:	B. Nguyen, P. Yang
Customer:	Drinking Water Coordination Committee (SDB & EMRB) and Operation Division (D. Dobrin)

Objective

Use isotope labelled Glyphosate (N-phosphonomethyl glycine) and LC-MS to develop a method for the isotope dilution mass analysis of glyphosate in water and vegetation samples.

Background

Glyphosate and its metabolite, aminomethyl phosphonic acid (AMPA), have molecular structures similar to naturally occurring amino acids. Because of the high ionic strengths of these compounds, organic solvents cannot be used to extract them from environmental samples. This makes their analysis difficult, and subject to significant error. Various analytical methods have been reported for glyphosate and AMPA using GC or HPLC with various detectors including fluorescence and mass spectrometers (MS). To date, none of these methods employs Isotope Dilution MS (IDMS). To achieve the best data quality, IDMS was evaluated in this study – and was chosen for its ability to correct for errors in all stages of the analytical procedure.

Results

We developed and validated an isotope dilution mass analysis method for the analysis of glyphosate and its metabolite, aminomethyl phosphonic acid in environmental and vegetation samples by using $^{13}\text{C}^{15}\text{N}$ – labeled glyphosate and an HPLC/MS system. The method exhibited superior data quality and operational efficiency. Method detection limits using standard USEPA protocols for glyphosate and AMPA were 0.06 and 0.30 $\mu\text{g/L}$, respectively (water samples), and 0.11 and 0.53 $\mu\text{g/g}$, respectively (vegetation samples).

Current Status

The method is complete. It has been audited by the Quality Management Unit and is on-line (LSB Method Gly 3415). A manuscript describing the method and its characteristics was prepared and submitted to J. AOAC for publication.

III. Time-of-Flight MS Determination of Toxic Organics

Study Leader:	Eric Reiner [Dioxin & Toxic Organics Section]; LECO Instruments
Study Team:	Adrienne Boden, Karen MacPherson; John Carron [Physical Chemistry & Litigation Section]
Customer:	All customers of DTO Section

Objective

To investigate and optimize time of flight mass spectrometry for the analysis of toxic organic compounds in environmental samples.

Background

In order to increase selectivity and reduce sample preparation requirements, *Fast GC* has been investigated in the past few years. The majority of analytical methods in DTO have now been converted to *Fast GC* on microbore columns. Analysis times have been reduced by up to a factor of 5. Detection of *Fast GC* peaks at low picogram detection limits by conventional quadrupole or high resolution mass spectrometry (MS) is limited because of insufficient sensitivity (quadrupole) or slow MS scan speeds relative to the narrow GC peak widths (high resolution). Time-of-flight (TOF) mass spectrometers have the advantage of much faster scan rates at good sensitivity compared to conventional MS methods. Therefore, it is expected that the benefits of *Fast GC* can be extended much further by the use of TOF-MS detection.

Results

Two companies that manufacture TOF-MS instruments – Micromass and Leco – were sent test samples for analysis. Initial results are encouraging for many of the analytes selected. Problems encountered included variable sensitivity for some compound classes, especially higher boiling analytes and GC peak tailing for planar molecules like PAH with molecular weights greater than or equal to 252. Initial data indicate that most PCBs, OC Pesticides and PAH may be selectively determined in a single *Fast GC* analysis. Deconvolution of analyte peaks has been impressive using the Leco instrument. Micromass uses an alternate approach - a higher instrument resolution of 5000 compared to the unit resolution achievable by the Leco mass spectrometer. Neither instrument could meet the 1 pg detection limit required for all analytes tested.

Current Status

Samples have been sent for additional evaluation, which also included the Thermo Finnigan TOF-MS instrument. Manufacturers have been requested to change their instrument designs to allow for operation of the transfer-line and ion source at higher temperatures – which we feel will reduce GC peak tailing. This should improve detection limits and allow for a better evaluation of the mass spectrometers. Preliminary results indicate that GC/TOF-MS may be able to achieve the required DQOs for the analysis of environmental samples.

IV. Pressurized Fluid Extraction Studies

Study Leader:	Adrienne Boden [Dioxin & Toxic Organics Section]
Study Team:	Rob Brunato, Dallas Takeuchi, Vin Khurana
Customer:	All customers of DTO Section

Objectives

To develop a method for the automatic extraction of sediment, vegetation and biota samples for toxic organic analytes, and to replace an aging Zymate Robot.

Background

Extraction of solid sample types can be difficult because solids often have variable organic carbon and moisture content, and are more subject to matrix effects than water or air sample types. Pressurized Fluid Extraction with the Automated Solvent Extractor (ASE) was evaluated and optimized for solid sample types.

Results

The ASE extractor has been optimized for the extraction of PAH and PCB/OC pesticides from solid sample types. The current work was focussed on optimizing extractions of solids for the chlorinated dioxins, and on comparing data with other extraction methods like sonication and microwave extraction. Sample extract cleanup for PAH directly in the extraction cell was investigated.

Current Status

Initial studies indicate that sample preparation directly in the ASE cell may be possible. Current problems include: backwash of sample extract up the delivery tube due to the lack of pressure release when the cell is rinsed.

V. ICP-MS Analysis of Road Dust for Trace Metals

Study Leader:	Mark Powell [Spectroscopy Section]
Study Team:	Lian Liu, Nada Gnanalingam, Lorraine Peters
Customer:	Steve Elliot and Mike Ladoucer [Eastern Region]

Objective

The objective was to develop an analytical method to support a project which uses concentration data to produce information about specific trace metals and by-products emitted from a site specific source as deposition in road dust. These measurements will be used to assess the inhalation of contaminants by residents in the community and support a risk- assessment study of the area.

Background

A road dust survey was initiated by the MOE - Eastern Region Air Quality Management Group to monitor the concentrations of arsenic, strontium, thorium and uranium emitted from a refinery as deposition to road dust. MOE is currently developing a standard under Regulation 346 for uranium in air. MOE-LSB has supported this study by developing an analytical method for the determination of these specific trace metals in road dust. Several spectroscopic techniques exist that could be used for this application, however, only ICP-MS appears able to quantify thorium at the trace concentrations required. It was also desired to determine all analytes simultaneously in a single analysis.

Results

A simple open vessel wet digestion using nitric acid was developed to dissolve road dust samples for ICP-MS analysis. A characterization was done on a representative sample to determine levels of spectral and chemical interferences on target elements. This information was used during method development to establish compromise operating conditions, interference corrections and initial dilution factors for samples.

Detection limits were determined to be in the low ppb range – which meets all

Data Quality Objectives (DQOs) for this specific application. Good accuracy and precision was shown with the available CRM representing a soil matrix. However, acquiring a reference material with certified concentrations of thorium and uranium in a representative matrix is necessary to achieve the data quality required before results generated by using this method can be considered as being more than semi-quantitative.

Current Status

This project is complete. The method RDUST E3423 (Trace Metals in Road Dust) has been written and an audit has been conducted by the QMU of LSB. The method is now in LIMS and on-line.

B. Methods Development

Introduction

Most method development work this year was directed to the determination of various organic analytes in air, water, soil, and fish. Only two projects involved new methods for individual compounds: MMT in drinking water and formaldehyde in drinking water – all of the other projects involved methods for the determination of a suite of compounds such as total petroleum hydrocarbons in water, volatile polar organics in air, and the mixed brominated/chlorinated dibenzo-p-dioxins and dibenzofurans. Although most of the method development work reported is based on mass spectrometry detection, the chromatographic separation is of critical importance in many of the methods. For example, methods for PAH, the dioxin-like PCBs, and the congener-specific toxaphenes, depend on the ability of GC columns to separate groups of compounds having very similar structures.

One project involved the interpretation of GC-MS data to identify disinfection byproducts of water chlorination. For this work, first principles of organic chemistry and mass spectrometry were used to piece together molecular structures like a jigsaw puzzle. This work is essential before routine quantitative methods can be developed, and illustrates the importance of fundamental knowledge to the solution of novel analytical challenges.

I. Reversed Phase & Ion-Pairing Determination of Diquat and Paraquat by LC/MS

Study Leader:	Lorna Grey [Applied Chromatography Section]
Study Team:	Bick Nguyen, Paul Yang
Customer:	John Hatton - Pesticide Analysis Lead [Operations Division]

Objective

To improve the Applied Chromatography Section's current LC/ESI-IDMS method for paraquat and diquat (PQDQ) analysis of environmental waters and vegetation samples.

Background

The two most important compounds in the bipyridylium class of herbicides are paraquat (PQ) and diquat (DQ), both of which are contact herbicides that damage plant tissues quickly, by way of cell membrane destruction. The determination of PQDQ in environmental water and vegetation samples is usually done by ion-pair HPLC -UV chromatography in a single analysis in which they are only partially resolved. Though the UV spectra for paraquat and diquat are very different, there is, nevertheless some overlap in absorbances from each of the compounds at the recommended wavelengths for quantitation. While this is an acceptable method (US EPA 549.1), the use of current chromatographic techniques can result in a method with much improved separation of PQ and DQ.

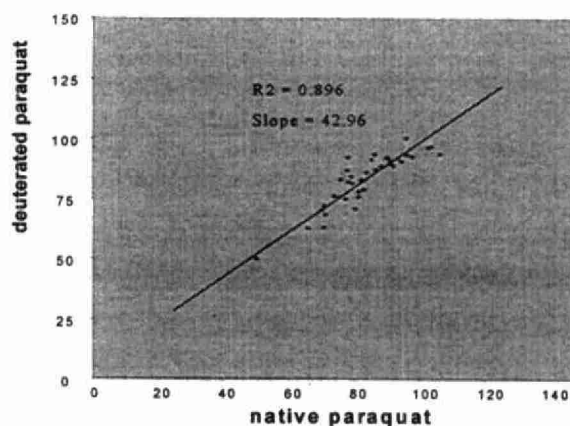
One important problem we found with this specific method is that pH manipulation of the matrix had a very profound effect on ^{13}C -diquat (surrogate for DQ) recovery. Even with little delay between pH adjustment of the sample and sample extraction, the ^{13}C -DQ recovery was very low. In situations where the sample was extracted quickly after pH modification, recovery of the target compound – native DQ (n-DQ) – was not adversely affected but remained stable at approximately 80%. The poor recovery of n-DQ with respect to ^{13}C -DQ was unacceptable, as the surrogate recovery was used to determine the concentration of native DQ in the original sample.

Several adjustments to the original PQDQ method for water and vegetation analysis were made. A major adjustment was to move from UV detection to MS/electrospray ionization (ESI) detection. Another was to use a method which did not require ion-pairing methodology. The traditional method requires that a non-volatile ion-pairing reagent be used both in the sample extraction procedure and the LC mobile phase. Unfortunately, non-volatile ion pairing reagents are not conducive to MS/ESI analysis as they lower the response of the MS signal, and cause significant contamination of the MS ion source.

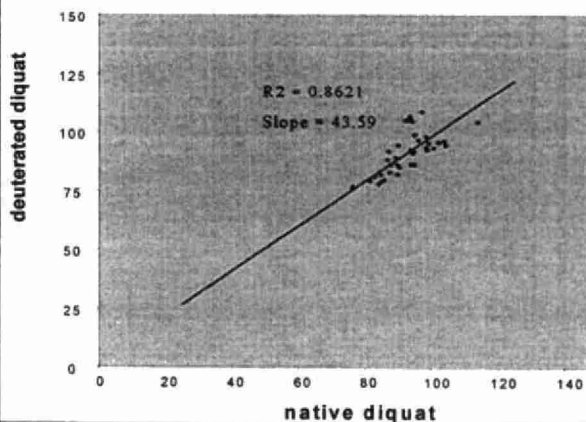
Results

The effect of these changes has resulted in baseline resolution of all the analytes including the surrogate analytes and has thus improved the identification and quantitation of PQDQ. Unlike UV detection, with MS detection and single ion monitoring (SIM) the quantitation of one analyte is not influenced by the presence of the other. The extraction procedure has been modified such that sample pH adjustment and the use of costly, non-volatile ion-pairing reagents are no longer necessary. The recovery of the target and surrogate analytes are enhanced or maintained at an acceptable level. This is achieved using Waters® Oasis® MCX extraction cartridges. These cartridges contain a mixed-mode sorbent with both reversed phase and cationic functionalities. The procedure does not require the use of separate ion-pairing salts for the sample

Correlation of % Recovery - deuterated vs native paraquat



Correlation of % Recovery - deuterated vs native diquat



extraction as strong cation sulfonic acid groups are attached to the surface of the sorbent polymer.

The new LC/ESI-IDMS PQDQ method yields an average recovery of $90 \pm 10\%$ for each analyte. Excellent correlation was obtained between the recovery of the native and isotope labeled surrogate of each analyte from a specific matrix (see graph).

Current Status

Method development studies have been completed, and the new LC/ESI-IDMS method is currently on-line.

II. Method for Dioxin-like PCBs in Environmental Samples

Study Leader:	K. MacPherson [Dioxins & Toxic Organics Section]
Study Team:	T.Kolic, V.Khurana
Customer:	Environmental Monitoring and Reporting Branch (Fish Contaminants & Surface Water)

Objective

To develop a method based on isotope dilution mass spectrometry, for the determination of the Dioxin-Like PCB congeners at ultratrace (ppt, ppq) concentrations in environmental samples.

Background

In 1998 the World Health Organization (WHO) identified 12 PCBs as demonstrating "dioxin-like" toxicological effects. These 12 congeners are collectively

referred to as Dioxin-Like PCBs (DLPCBs). The MOE method for the determination of Dioxins/Furans in environmental samples reports concentrations for the 17 individual Dioxin/Furan congeners which have been assigned Toxicity Equivalency Factors (TEFs) by the World Health Organization (WHO). WHO has also designated TEFs for 12 of the 209 PCB congeners, to allow PCBs to be reported as 2378-TCDD toxic equivalents – which presents a much better estimation of the toxicity of the sample. The dioxin method was modified to allow for the determination of these 12 PCB congeners. With this method, congener-specific data for Dioxins/Furans and DLPCBs can be reported from the same sample.

Results

The method for the determination of DLPCBs (MOE LIMS Method Product Code DFPCB 3418) received CAEAL accreditation in May, 2000. The MOE Dioxin Laboratory was the first in Canada to receive CAEAL accreditation for these compounds. As part of this overall effort, MOE-LSB also produced the first certified soil reference material for DLPCBs. Consensus value concentrations for this reference material were determined through an international round-robin study.

Current Status

The method has completed an internal QMU audit, received CAEAL accreditation and is online.

Publications and Presentations

K.A. MacPherson, T.M. Kolic, E.J. Reiner, V.K. Khurana. Method for Congener-Specific Determination of Dioxin-Like PCBs in Biota and Soil/Sediments. *Organohalogen Compounds* **1999**, 40, 193-196 [*presented at 19th International Symposium on Halogenated Environmental Organic Pollutants and POPs, Venice, Italy, September 13, 1999*].

S.S. Selliah, S. Cussion, K.A. MacPherson, E.J. Reiner and D. Toner. A Reference Material for Routine Performance Monitoring of Methods Measuring Dioxin-Like Compounds in Solid Matrices. *Organohalogen Compounds* **2000**, 45, 156 - 159 [*Presented at 20th International Symposium on Halogenated Environmental Organic*

Pollutants and POPs, Monterey, California, August, 2000].

T.M. Kolic, K.A. MacPherson, E.J. Reiner, T.Gobran and A. Hayton. A Comparison of TEQ Contributions From Chlorinated Dioxins, Furans and Dioxin-Like PCBs in Great Lakes Fish. *Organohalogen Compounds* **2000**, 46, 562 - 565 [*Presented at 20th International Symposium o Halogenated Environmental Organic Pollutants and POPs, Monterey, California, August, 2000*].

S.S. Selliah, S. Cussion, K.A. MacPherson, E.J. Reiner. And D. Toner. Development of a Reference Material for Routine Performance Monitoring of Methods Measuring Polychlorinated Dibenzo-p-Dioxins, Polychlorinated Dibenzofurans and Dioxin-Like Polychlorinated Biphenyls. *Fresenius Journal of Analytical Chemistry*, *in press*.

III. Method for PAH in Soil, Sediment and Biota by Isotope Dilution GC-MS

Study Leader:	Adrienne Boden [Dioxin and Toxic Organics Section]
Study Team:	John Bodnar, Eric Reiner
Customer:	Standards Development Branch (Phytotoxicology), Region Operations Division and Environmental Monitoring and Reporting Branch (Surface Water Surveillance)

Objective

To develop an isotope-dilution, high resolution mass spectrometer (HRMS) method for the determination of polycyclic aromatic hydrocarbons (PAH) in soil, sediment and biota. This new method will use isotopically-labelled analogues of the PAH of interest to compensate for variable recovery of PAH during sample pretreatment and for the effects of instrumental variables.

Background

Polycyclic aromatic hydrocarbons are one of the largest single classes of chemical carcinogens known today. PAH are formed during the incomplete combustion

of carbon-based fuels and have been found to be ubiquitous environmental pollutants. In order to meet data quality objectives (DQOs) in the determination of PAH in environmental samples, lower limits of detection are required while maintaining acceptable precision and accuracy levels. While the attainment of sensitivity and instrumental precision is quite easy using today's GC-MS instrumentation, the accuracy of quantitative data often suffers at the hand of sample losses during extraction, clean-up procedures and general sample handling in the laboratory.

The capability of the mass spectrometer to distinguish stable isotopes also allows for the use of stable isotope-labelled analogues of individual analytes as internal standards in quantitative assays, a technique referred to as "isotope dilution". An isotope-dilution GC-MS method was adopted in order to quantify each analyte against their isotope-labelled analogues as well as correct for analyte recovery during sample preparation and analysis. The isotopically-labelled internal standards can significantly reduce systematic error (bias) from several sources including sample stability prior to analysis, analyte loss during both the extraction procedure and post-extraction sample workup and from the calibration procedure.

This new method is designed to replace the current LSB method E3350. Method E3350 utilizes: (i) a lengthy sonication/robotic extraction procedure requiring large amounts of solvent, (ii) manual nitrogen evaporating steps, (iii) a single-point calibration, and (iv) does not account for analyte recovery in the quantification of all PAH. This new method utilizes: (i) a rapid accelerated solvent extraction system with low solvent consumption, (ii) a Zymark turbovap evaporating system, (iii) a multi-point automatic calibration method, (iv) an isotope-dilution method which inherently tracks and corrects for method recovery during all steps of sample preparation and analysis for all PAH, and (v) an automatic quantification/reporting method which also tracks quality control data.

Results

Method development was expanded to include replacement of the ultrasonic extraction/Zymark robotic sample preparation method by the Pressurized Fluid Extraction technique, which is a sample extraction technology that combines elevated temperatures and pressures with liquid solvents to achieve rapid removal of analytes from various samples (see p. 9 of this report). The entire extraction procedure is fully

automated and performed in minutes. This procedure was adopted for its speed, simplicity, reduction in sample handling, savings in labour, equipment and bench space and low solvent requirements.

Sample analysis & quantification was revamped to include new GC-MS data acquisition methods and a multi-point calibration technique (replacing the current single-point method). A new GC-MS continuing calibration method to assess instrumental performance has also been employed. Automatic data analysis and data reporting methods were developed to enhance the reporting of PAH and QC data. Overall, the new method will improve the accuracy of PAH data produced and significantly reduce the time required for extraction and sample preparation.

Current Status

Method development for all items described above has been completed. Performance data for method validation are currently being produced. This method and its predecessor (MOE method E3350) are being run in parallel as a part of the validation prior to replacement of method E3350. The new method will be available for use by the Fall of 2001. Future work includes the investigation of clean-up methods incorporated into the extraction step, and the optimization of the GC-MS step – possibly including the use of fast-GC methods.

IV. Method for Formaldehyde in Drinking Water

Study Leader:	Steve Jenkins [Mass Spectrometry Section]
Customer:	Operations Division

Objective

To develop a method for the quantitative analysis of formaldehyde in surface, ground, and drinking waters. The method was designed to meet the Interim Provincial Water Quality Objective of 0.8 ug/L.

Background

A request had been made to analyse leachate – which included formaldehyde – from a commercial wood chip pile. Formaldehyde was used as a mobility indicator of the leachate, and there was concern that the leachate may contaminate local surface waters.

Results

The formaldehyde in water is reacted with acidic 2,4-dinitrophenylhydrazine to form the hydrazone derivative. The derivative is extracted with hexane, the extract evaporated to dryness and taken up in dichloromethane. Analysis is done by GC/selected ion monitoring MS (quadrupole MSD). The method has a detection limit of 0.3 ug/L.

Current Status

The method has been completed.

V. Evaluation of Analytical Methods to Support the Toxicity Characteristic Leaching Procedure (TCLP)

Study Leader:	John Carron [Physical Chemistry & Litigation Section]
Customer:	Standards Development Branch/Waste Management

Objective

To provide the Branch with the capability to analyze leachates produced by using the EPA Method 1311, Toxicity Characteristic Leaching Procedure (TCLP) for organic and inorganic parameters. The use of the TCLP Zero Headspace Extractor for volatile organic compounds and the suitability of the current LSB analytical methods to analyze TCLP leachates for the new Schedule 4 parameter list in the proposed revision to Ontario Regulation 347 were investigated in this project. The new regulation will come into effect, 1 April, 2001 as Ontario Regulation 558-00.

Background

The Environmental Protection Act Regulation 347 defines "hazardous waste" as a waste that is a *leachate toxic waste*. Two of the three proposed changes to this regulation include a "derived from" rule, and a new TCLP process and analysis of the leachate for an expanded list (88 contaminants) of organic and inorganic chemicals. The TCLP process proposed is similar to EPA method 1311. The expanded list of chemicals includes many volatiles and semi volatiles such as pesticides and herbicides. These changes will make the regulation consistent with current rules set by the US EPA and provide clear information to the public as well as the handlers and generators of hazardous waste.

Results

Standards were custom prepared by Protocol Analytical Supplies Inc. The large number of chemicals listed in Regulation 347, and their high concentration levels, necessitated that several different TCLP spiking solutions be prepared. Five samples

that contained high metal concentrations were used to produce TCLP leachates for analytical evaluation studies. Portions of the leachate were spiked with different mixes of the TCLP metals and semi volatile organics at mg/L concentrations. The suitability of LSB methods to provide leachate analyses will be evaluated by the percent recovery of spikes and by the analytical precision. Initially, acceptable performance criteria will include 50% spike recoveries and a maximum 50% relative standard deviation (%RSD).

Volatile spikes in waste leachate and additional spiked solid samples extracted using the Zero Headspace Extractor (ZHE) were analysed using two different instruments. A data comparison between the Headspace Capillary Gas Chromatography using Flame Ionization Detection Electron Capture Detection (H/S-GC-FID/ECD) and Purge and Trap Capillary Gas Chromatography using Mass Spectrometry (P/T-GC-MSD), was performed. The TCLP extraction procedure has also been applied to three in-house metal reference dust samples. Results have been compared to historical data that employed the Regulation 347 leach extraction procedure. No work has been done using barium (100 ppm) and boron (500 ppm) because of the high concentrations involved.

The raw (unprocessed) leachate extracts were provided to an instrument manufacturer for analysis using this extract by GC/Time-of-Flight Mass Spectrometry (TOFMS). Good results for 41 of the 54 required organic analytes were achieved with no sample clean-up. This approach suggests that one instrument may be able to provided all required TCLP organic analyses which presently requires at least six different methods.

Current Status

With a few exceptions, metal and volatile analyses are complete. Data have been tabulated and evaluated for these results. Of the 88 parameters in the schedule 4 list of contaminants, the following parameters have not been included in this study: barium, boron, silver, and vinyl chloride. In addition, LSB has no current approved method for methyl ethyl ketone, pyridine, and nitrobenzene. To date, results for 12% of the analytes are still outstanding. A completed analytical process for TCLP extracts is targeted for spring 2001. A sampling and analysis guide for waste sampling, intended for the TCLP leachate method, is in progress. Janet Mills, Ijaz Ahmad and John Carron are preparing the first edition, expected by spring, 2001.

VI. Identification of Water Disinfection Byproducts

Study Leader:	Vince Taguchi [Mass Spectrometry Section]
Customer:	Environmental Monitoring and Reporting Branch, Standards Development Branch

Objective

To identify disinfection by-products (DBPs) in treated drinking water using advanced mass spectrometric techniques.

Background

The chlorination of drinking water results in the formation of DBPs from the reaction of the chlorinating agents on the natural organic content of the raw water. In addition to the common DBPs such as trihalomethanes (THMs), a number of DBPs which could not be identified by library searching techniques have been detected in the characterization (identification) of extractable organics (product code EXT3186). Most of these were listed as compound classes, i.e. chlorinated DBP, brominated DBP. This project was initiated as a followup to identify 2 of these DBPs which were detected in approximate concentrations ranging from low $\mu\text{g/L}$ to hundreds of $\mu\text{g/L}$.

Results

The EI mass spectra of the 2 major DBPs in the extracts contained mono-chlorinated and mono-brominated ions at m/z 107/109 and m/z 151/153 respectively as well as ions at m/z 31, 43, 59 and 71 that were common to both DBPs. Library searching techniques on the HP 5970/ 5973 MSDs suggested mono-halogenated butanol structures but no credible matches could be found. Positive ion CI spectra obtained with methane as the reagent gas on the VG Trio-2 contained mono-chlorinated and mono-brominated ions at m/z 105/107 and m/z 149/151 respectively, 2 Thomsons lower than in their corresponding EI spectra. No $M+H^+$ ions were initially observed. Accurate mass measurements on the VG ZAB-2F HRMS confirmed the empirical formulae for the significant ions in the EI spectra and the mono-halogenated

butanol structures. Further CI experiments with other reagent gases on the VG Trio-2 and on the Finnigan MAT TSQ-70 revealed possible molecular weights of 139 and 183 Da respectively. MS/MS experiments (product ion scans from specified precursor ions and precursor ion scans for specified product ions) in EI and CI on the TSQ-70 were used to elucidate the fragmentation schemes. The two compounds have been tentatively identified as 1-aminoxy-1-chlorobutan-2-ol and 1-aminoxy-1-bromobutan-2-ol respectively. These are the first DBPs having the aminoxy- structure to be identified in treated drinking water. Confirmation of these structures with their absolute configurations would require unambiguous syntheses and comparison of their accurate mass and MS/MS data.

Current Status

A paper entitled "Structural Elucidation of Disinfection By-products in Treated Drinking Water" was submitted to "Rapid Communications in Mass Spectrometry" on December 18, 2000. It was accepted for publication on January 31, 2001 and is currently *in press*.

VII. ppq Determination of PCB Congeners, Organochlorines & PAHs by GC/MS

Study Leader:	Stephanie Lemanik [Applied Chromatography Section]
Study Team:	Christy Hartley, Paul Yang
Customer:	Duncan Boyd [Environmental Monitoring & Reporting Branch]

Objective

To develop a gas chromatography - mass spectrometry (GC-MS) method for the analysis of persistent organic pollutants, e.g. polychlorinated biphenyl (PCB) congeners, organochlorines (OCs), chlorobenzenes (CBs) and polycyclic aromatic hydrocarbon (PAH), with part-per-quadrillion (ppq) detection limits.

Background

Customers at the Environmental Reporting and Monitoring Branch requested a method capable of the determination of individual PCB congeners, OCs, CBs and PAH at the ppq level with good data quality and low operating costs. With the data quality objectives provided and resources available, it was decided that the use of a bench-top GC/MS with large volume sample preparation methods would be the best approach.

Results

By using solid phase extraction and an Agilent 6890 GC and 5973 MSD, a method capable of analyzing 103 target compounds at the high ppq level was developed. Typical detection limits for selected PCB congeners, PAHs, and organochlorines are listed in the Table below.

Compound Name	Std. Dev., ng/L (N = 10)	W , ng/L
PCB Congeners		
PCB 28 (2,4,4'-)	0.17	0.2
PCB 77 (3,3',4,4'-)	0.72	0.5
PCB 128 (2,2',3,3',4,4'-)	0.64	0.5
PCB 169 (3,3',4,4',5,5'-)	0.45	0.5
PCB 105 (2,3,3',4,4'-)	0.25	0.2
PCB 118 (2,3',4,4',5-)	0.22	0.2
PCB 123 (2',3,4,4',5-)	0.18	0.2
PCB 156 (2,3,3',4,4',5-)	0.26	0.2
PCB 157(2,3,3',4,4',5'-)	0.28	0.2
PCB 167 (2,3',4,4',5,5-)	0.27	0.2
PCB 189(2,3,3',4,4',5,5'-)	0.26	0.2
Polycyclic aromatic hydrocarbons		
Benzo[a]pyrene	0.72	0.5
Benzo[g,h,i]perylene	0.81	0.5
Organochlorines		
γ-chlordane	0.61	0.5
Mirex	0.55	0.2

Current Status

The method will be further improved using either deuterium or ^{13}C -labelled isotopes as internal standards. By use of an internal standard method, it is likely that the method precision will be improved, and thus the method detection limit.

VIII. Determination of Mixed Brominated Diphenyl Ethers

Study Leader:	Karen MacPherson [Dioxin & Toxic Organics Section]
Study Team:	Terry Kolic, Eric Reiner
Customer:	Environmental Monitoring & Reporting Branch

Objective

To develop an isotope dilution method for the determination of specific Brominated Diphenyl Ethers.

Background

International concern over Brominated Diphenyl Ethers (BDEs), used world-wide as flame retardants, originates from the fact that concentrations are increasing – contrary to most persistent organic pollutants (POPs). For example, one Swedish study showed concentrations of BDEs in human breast milk have doubled every 5 years. A number of countries have reported BDE levels in human blood serum and breast milk samples. Recently, BDEs have been found in Canadian breast milk samples. In general, the relative congener concentrations in Canada were comparable to those reported elsewhere in the world, but do exhibit regional variations. There are limited data for North American concentrations in commercial food, human intake/uptake and body burdens, relative to the European countries.

The need to assess potential risks of BDEs to humans and the environment is urgent due to their ubiquitous environmental occurrence, bioaccumulation tendencies, and perceived rate of increase.

Results

There exists a lack of commercially available standards and reference materials with certified concentrations for BDEs. A set of calibration series standard mixes were obtained from Wellington Laboratories, which contained the most predominant BDE congeners (based on relative concentration and environmental occurrence) and their $^{13}\text{C}_{12}$ – analogs. A preliminary investigation for the determination of BDEs was carried out using the mono-ortho fraction of the DLPCB extract for various samples, by using LSB Method DLPCB3418. Results for MOE reference material RM9801– a potential fish reference material MOE FISH – and an existing reference material CIL EDF-2525 (BDE values not certified or otherwise reported) are shown in Table I.

Table I – Reference Materials BDE results

Compound	MOE LSBRM9801 (pg/g) N=2	MOE FISH (pg/g) N=1	CIL EDF-2525 (pg/g) N=1
BDE 28	2	3000	200
BDE 47	500	100000	10000
BDE 99	200	10000	1000
BDE 153	1	5000	2000
BDE 154	2	3000	2000
BDE 183	2	30	70

Current Status

Future studies will incorporate a series of calibration standards for isotope dilution quantification techniques as part of the ongoing development of a routine method for the determination of BDEs in environmental samples.

Publication

MacPherson, K.A., Reiner, E.J., Kolic, T. And Khurana, V. An Investigation of reference materials for Brominated Flame Retardants. *Organohalogen Compounds* **2000**, 47, 222-224.

IX. Congener-Specific Toxaphene Determination

Study Leader:	Tony Chen [Dioxin & Toxic Organics Section]
Study Team:	Mary Ann Bogard, Corina Lucaciu, Sanja, Lucic, Eric Reiner
Customer:	Alan Hayton [Environmental Monitoring & Reporting Branch]

Objective

To develop a congener-specific analytical method for the 22 toxic Toxaphene congeners in solid sample types.

Background

Toxaphene consists of up to 650 congeners, and was used widely until the late 1970s. The environmental pattern of Toxaphene is altered considerably by the weathering process. Because of weathering, only a subset of the original congeners released to the environment can be detected; these include the 22 toxic congeners.

Results

Standards have been purchased. Calibration curves have been developed and the chromatography of the 22 congeners has been characterized and optimized using Fast GC.

Current Status

The method is almost complete. Round robin samples have been analysed and the group is waiting for results. MDLs for spiked samples need to be completed. There are no reference materials for this group of compounds. We are investigating exchange of samples with other laboratories as part of the final method validation.

X. GC/MS Determination of 3-chloro-4-dichloromethyl-5-hydroxy-2(5H)-furanone in Drinking Water

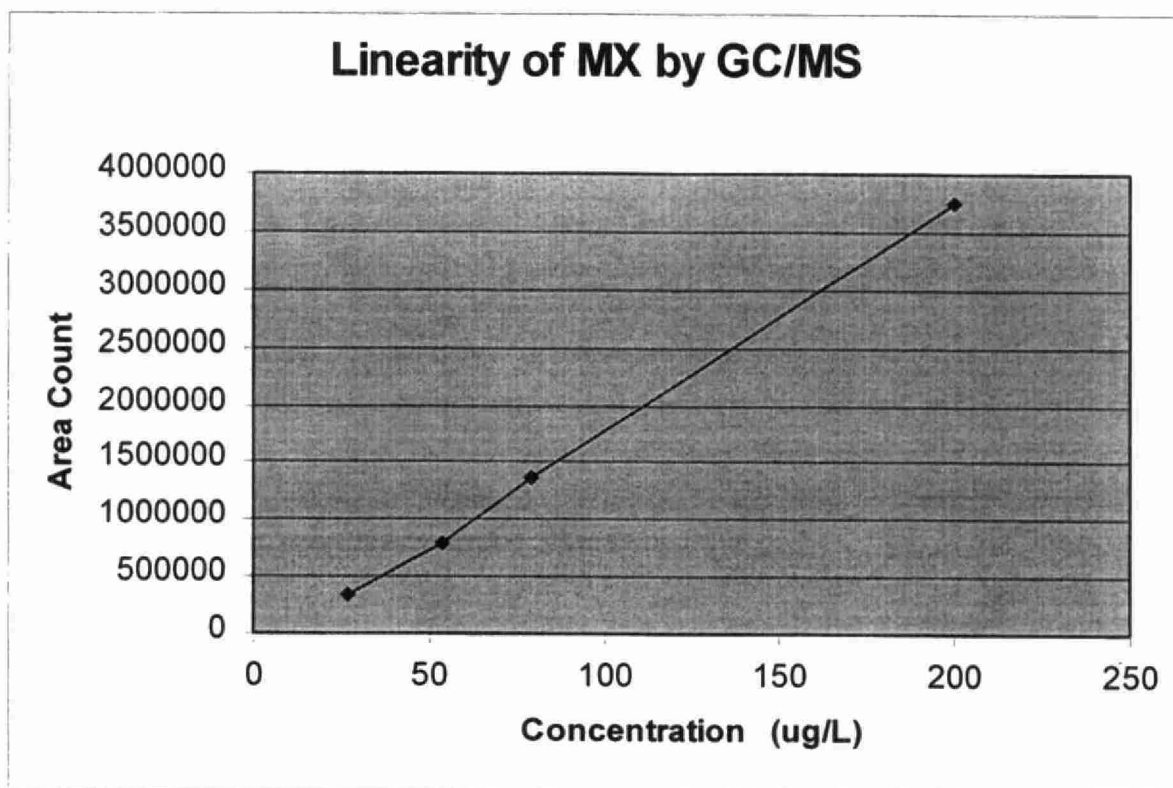
Study Leader:	Larry Matchuk [Applied Chromatography Section]
Study Team:	Paul Yang
Customer:	Drinking Water Coordination Committee (SDB & EMRB) and D. Dobrin [Operations Division]

Objective

To develop a routine analytical method for the monitoring of the chlorine disinfection byproduct (DBP) 3-chloro-4-dichloromethyl-5-hydroxy-2(5H)-furanone.

Background

Chlorination has long been an important part of the water treatment process to ensure the elimination of microbial hazards. The chlorination of organic substances present in water systems has resulted in the production of numerous DBPs, but many have yet to be detected or characterized. Some, such as the trihalomethanes (THMs), are known to be carcinogenic to laboratory mammals, although at doses far greater than human intakes from drinking water. The compound 3-chloro-4-dichloromethyl-5-hydroxy-2(5H)-furanone (MX) was shown to be genotoxic in the Ames test (a bacterial system). In fact, the identification of MX made up 30% of the previously unexplained



total genotoxicity of extracted DBPs. The Applied Chromatography Section (AC) has been analyzing haloacetic acid DBPs in drinking water samples using method E3383. Using the same procedures listed in method E3383 to analyze MX, if validated, would present a logical and efficient approach to the monitoring of this important DBP.

Results

Using method E3383, the linearity and detection limit for MX were determined. Analytical data are shown in the Figure (above) and Table (below).

Method Performance (N = 10)

Compound Name	Spiked	Recovery, Average	% Recovery	Std Dev	W	MDL*
	$\mu\text{g/L}$			$\mu\text{g/L}$		
3-chloro-4-dichloromethyl-5-hydroxy-2(5H)-furanone	54	48.3	89.4	1.94	4.01	5.46

* MDL calculated using a Students' T value of 2.821 @ 99% confidence level

Current Status

A 2.5-month field study to validate the method is scheduled to start March 2001. Upon completing the field study and documentation of the performance data in the method we plan to analyze and report this compound using method E3383.

C. Analytical Reference Activities

The broader focus of this section is intended to capture the wide range of significant activities, in addition to collaborative projects with outside groups, that the Laboratory Services Branch performs. The majority of these activities involve development and evaluation of commercial instrumentation or products, external laboratory evaluations and assistance, and communication/technology transfer actions.

I. Evaluation of GC and HPLC Columns for Organic Analytes Determination

LSB Study Team:	Karen MacPherson, Tony Chen, Adrienne Boden, Eric Reiner [Dioxin & Toxic Organics Section]; Paul Yang [Applied Chromatography Section]
Collaboration with:	Restek Corporation, Bellefonte, P.A

Work this year was spent in attempting to develop a column capable of complete and unequivocal separation of all 17 of the 2,3,7,8-substituted chlorinated dibenzo-p-dioxins and dibenzofurans from the group of 210 dioxins/furans. It was hoped that by studying various combinations of phases and columns, one could be found to achieve this separation. Although columns have been made that have improved performance, it may not be possible to achieve complete separation by using currently available phases.

In addition, Restek staff have worked with Paul Yang on the development of microbore HPLC columns for LC-MS applications. Because of the small amounts of analyte required and the high efficiency of microbore columns, peak shapes are very narrow, which permits much improved separation of sample components. This will lead to significant improvements in the identification of sample components that will be beneficial to all environmental laboratories.

II. Development of Environmental Reference Materials

LSB Study Team:	Sathi Selliah [Quality Management Unit]; Eric Reiner [Dioxin & Toxic Organics Section]
Collaboration with:	Brock Chittim [Wellington Laboratories]

Reference materials as well as lab standards are required for the accurate determination of contaminants in complex environmental samples. A shortage of such reference materials exists for sample types such as sediment and fish. Last year, the production of a candidate sediment reference material for the Chlorinated Dioxins/Dibenzofurans (PCDDs/PCDFs) and the dioxin-like PCBs (DL-PCBs) was reported. This year an international round-robin study was completed to generate consensus-value concentrations of the PCDDs/PCDFs and DL-PCBs, and the sediment was sold to Wellington Laboratories for marketing to the international scientific community. A second potential reference material, freeze-dried fish, has been identified. Homogenization of this material was completed, and it is ready to be distributed in a round-robin study to generate consensus concentration values of selected analytes.

III. Mass Spectrometry Discussion Group

LSB Leader:	Vince Taguchi [Mass Spectrometry Section]
Collaboration with:	Toronto Area Mass Spectrometry Discussion Group

The Laboratory Services Branch (LSB) supports communication activities between analytical professional in Ontario. For the past few years, LSB has been the site of the regular meetings of the *Toronto Area Mass Spectrometry Discussion Group*. Organized by Dr. Vince Taguchi, six evening seminars were held during 2000 in the 125 Resources Road auditorium. The distinguished lineup of speakers and their topics of discussion were:

- ☐ Professor Johan K. Terlouw, McMaster University. *The Interpretation of EI Mass Spectra and the Concept of Proton Transport Catalysis* [February 22].
- ☐ Dr. Gary Kruppa, Bruker Daltonics. *Applications of Accurate Mass MS/MS and New Dissociation Methods using FTMS* [March 22].
- ☐ Dr. Mehran Alaei, National Water Research Institute. *Mass Spectrometry Challenges of Analyzing Brominated Flame Retardants* [April 18].

- Professor Ken Marcus, Clemson University. *True Elemental Speciation in Liquid Chromatography through Particle Beam – Glow Discharge Mass and Optical Spectrometries* [May 25]
- Dr. T.A. Jackson, National Water Research Institute. *Systematic Variations in the Stable Isotope Composition of Mercury in Mercury-Polluted Freshwater Ecosystems* [November 2].
- Dr. Robert Cody, JEOL USA, Inc. *What to do with Slow Electrons: Gas-Phase Electrochemistry and Other Experiments* [November 28].

For notices of upcoming seminars, those interested should check the internet site:
www.csms.inter.ab.ca

IV. Evaluation of Valco Pulsed Discharge Detector

LSB Leader:	Gerry Ladwig [Dioxin & Toxic Organics Section]
Collaboration with:	Gordon McFarlane [Valco Instruments]

Laboratory Services Branch staff on occasion work with instrument manufacturers to evaluate new technologies for environmental analysis applications. The Pulsed Discharge Detector (PDD) is being evaluated as a possible replacement for ECD detectors. The main advantages of a PDD over ECD are that it is non-radioactive, multi-modal (HID, PID and ECD modes), capable of sub-picogram sensitivity and has a linear dynamic range over 4 orders of magnitude. To date, results look promising. The initial instrument configuration was chosen to duplicate as closely as possible the current Fast-GC analysis as performed in our lab. Standard comparisons to date on both PDD and ECD have found better sensitivity on ECD to the sub-picogram range, with the PDD reaching low picogram levels. Efforts to improve PDD sensitivity have included switching controller electronics, installation of a heated gas purifier on dopant gas and detector substitution. Bias voltage instability was also evident during our trials. As detector sensitivity is one of several critical factors in trace-level analysis and is the main *raison d'être* for this detector, linearity and other studies have not been performed until resolution of the sensitivity issue. Our efforts will be continuing with the re-configuration of the instrument to a conventional GC analysis, instead of the Fast-GC configuration to address the sensitivity issue.

V. International Round-Robin Studies

LSB Leader:	Sylvia Cussion [Quality Management Unit]
Collaboration with:	various

A critical activity to benchmark laboratory performance against that of other international leaders, and to enhance an internal QA program, is activity in external round-robin studies. In the past year, LSB has participated in 39 such studies. International studies included four CRM certification studies from the Laboratory of the Government Chemist (LGC) in the UK, for Trace Metals and PAHs in Sewage Sludge and River Sediment. A round-robin for Trace Metals on Air Filters from the International Atomic Energy Agency (IAEA) involved MOE Methods E3277 and E3402. The General Chemistry and Microbiology Section and Spectroscopy Section participated in two different studies from Norway (water and precipitation sample types), and dioxins and dibenzofurans in fly ash for a study originating in Italy were determined by using MOE Method E3418 (Dioxin & Toxic Organics Section – DTO). In addition, the DTO Section participated in the 6th round-robin for soil and flyash samples from Umeå University (Sweden).

LSB was involved in the organization of an international round-robin study coordinated by Dr. Terry Bidleman of Environment Canada, which involved the evaluation of methods for toxaphene determination. Eleven laboratories participated (6 Canadian, 4 American, 1 Norwegian). Standards and an air sample extract were provided by Dr. Bidleman's laboratory. The solutions were ampouled by the QM Unit and distributed to the participants. Target compounds were Total Toxaphene and 7 Toxaphene congeners.

VI. Analytical Reference Assistance

LSB Leaders:	various
Collaboration with:	various

1. MOE requires the use of accredited labs for reporting data under the new Drinking Water Regulation 459/00. LSB supports this requirement through the provision of staff who act as assessors for the Canadian Association for Environmental Analytical Laboratories (CAEAL). The five staff who are certified

assessors are Cathy Doehler, George Steinke, Ann Jones, Dallas Takeuchi, and Cammy Mack. In addition, Cathy Doehler serves as a member of the CAEAL Advisory Panel. Because of the new water regulations, all of LSBs assessors found 2000 to be a very busy year.

2. Sylvia Cussion of the Quality Management Unit performed procedure audits and review of record keeping practices for all Master Stations and three satellite stations of the Integrated Atmospheric Deposition Network (IADN). These stations are located around the Great Lakes and monitor ambient air and precipitation for various toxics, including Trace Metals, PAHs, Organochlorine Pesticides, and PCB congeners. The eight stations audited were situated in Ontario, Michigan, Illinois, and New York.
3. LSB staff are often consulted regarding advice on selecting analytical methods for specific applications, on adapting methods for new uses, and on developing new methods. For example, Vince Taguchi and Patrick Crozier of the Mass Spectrometry Section have assisted Metro Works staff regarding the determination of the nonylphenol ethoxylates in sewage treatment plants. A significant level of assistance has also been given to Ontario microbiology laboratories by LSB's Senior Microbiology Scientist, Rhonda Schop. Increased testing of drinking water for microbiological parameters has resulted from Ontario's Walkerton incident, and Rhonda has provided significant private laboratory support in the form of advice on how to achieve consistent, high quality results.

Staff of LSB are sometimes called upon to investigate environmental laboratory data conflicts. In 2000, a regional laboratory was concerned about contracted analyses of drinking water samples for nitriloacetic acid (NTA) and nitrosodimethylamine (NDMA). LSB staff conducted a thorough review of the methodologies used, and suggested improvements to the contractor. After conducting method testing by use of performance evaluation samples, the data quality issues were resolved.

VII. International Laboratory Assistance

LSB Leaders:	Vince Taguchi [Mass Spectrometry Section]; Eric Reiner [Dioxin & Toxic Organics Section]
Collaboration with:	various

1. The State of California set a limit of 2 ng/L for NDMA in drinking water, but had difficulty finding laboratories who could achieve that limit of detection. They therefore were working under an interim guideline of 20 ng/L. Officials contacted Dr. Vince Taguchi of LSB's Mass Spectrometry (MS) section – because Vince had published an NDMA method capable of producing the detection levels required by California. After successfully completing analysis for a number of check samples, several California laboratories have adopted the MOE-LSB method. The MS Section has also acted as the high resolution mass spectrometer reference laboratory in a California Department of Health Services round-robin study.
2. As one of the world's leading Dioxin laboratories, the Dioxin Unit of the LSB – Toxic Organics and Dioxin Section periodically receive visiting delegations from other countries. In 2000, visitors from Japan, China, and Hong Kong toured the Dioxin Laboratory and requested information regarding analytical methods for the determination of toxic chemicals. From a request by the Hong Kong government for assistance, Dr. Eric Reiner visited their laboratory to perform an audit of their dioxin analysis methods. The Quality Management Unit provided performance evaluation samples to a Taiwan laboratory, which were reviewed by Sathi Selliah (QMU) and Eric Reiner. The Dioxin Unit also analyzed special study samples for Thailand.

VIII. EnviroAnalysis Conference Support

LSB Leader:	Ray Clement [Director's Office]
Collaboration with:	R. Burk [Carleton University]

The Third Biennial International Conference on Chemical Measurement and Monitoring of the Environment (*EnviroAnalysis 2000*) was held May 8-11 in Ottawa, ON. Some 300 delegates attended to learn of the latest environmental analytical

developments from 123 verbal and poster presentations. Ray Clement from the MOE-Laboratory Services Branch was co-chair and co-organizer of the conference, which also included analytical workshops held May 6-7. Published Proceedings from this conference are available from the Laboratory Services Branch library.

IX. Uncertainty Model for Dioxins/Furans/Dioxin-like PCBs in Soil & Sediment

Study Team:	George Steinke, Sathi Selliah [Quality Management Unit]; Eric Reiner, Karen MacPherson [Dioxin & Toxic Organics Section]
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Building on existing approaches to estimating analytical uncertainty in place within the Laboratory Services Branch (LSB), a rugged model was developed that allows the reporting of uncertainties associated with the analysis of 17 Dioxins/Furans and 12 Dioxin-like PCBs in soils/sediments. The model is compliant with the latest guidance from the international community. Inputs into the model included several international round-robin studies, method validation data, and a careful review of every aspect of the analytical procedure to identify and estimate significant sources of uncertainty. Including estimates of uncertainty with reported results is emerging as the reporting technique of choice, and a requirement under ISO accreditation, and LSB leadership in this area will benefit both the users and producers of analytical data.

D. LSB Seminar Series

Five seminars in the LSB 2000 Seminar Series covered a wide array of topics, from ICP-MS to Solid Phase Microextraction to the Safe Operation of Fume Hoods. The seminar speakers were all top experts in their respective fields, including two who have achieved international prominence for their achievements (Dr. W. Jennings and Prof. J. Pawliszyn). Seminars were well attended by not only LSB staff, but also by staff of external organizations. Brief descriptions of the seminars held are given below.

I. Safe & Efficient Use of Laboratory Fume Hoods: Kevin J. Tinsley, Advanced HEPA Technologies Inc., February 9, 2000.

The various types of fume hoods and when each should be employed was discussed. Practical tips for safe operation including regular testing and troubleshooting were covered. This seminar was enjoyed by 35 laboratory staff, who found that proper fume hood operation was more complex than they had previously thought.

II. Optimized Peaks Separation by Getting Properly Connected in HPLC: Rick Hersom and Jaime Martain, Chromatography Sciences Company (CSC), March 23, 2000.

This combination seminar/hands-on workshop was attended by 31 staff in two sessions. Special fittings connector kits were used to show the difference between the quality of various combinations of HPLC connectors. By connecting fittings that had been cut into half, the presence or absence of dead volume – depending on the specific fittings used – could be clearly seen.

III. Improving Sample Throughput in the Environmental Laboratory Utilizing Inductively Coupled Plasma Mass Spectrometry (ICP-MS): Elzbieta (Ela) Bakowska, Agilent Technologies, April 18, 2000.

About 25 staff discovered the latest developments in automated instrumentation for high throughput ICP-MS analysis including automatic on-line addition of internal standards, and on-line dilution of samples with severe matrix suppression. Several techniques for improving overall laboratory productivity were discussed.

IV. Analytical Gas Chromatography: Walter Jennings, Agilent Technologies, October 4, 2000.

Dr. Jennings began by examining some apparent anomalies in gas chromatography, and then expanded these considerations into a clearer understanding of how to manipulate and apply some basic design and operational parameters to achieve good performance. Over 40 attendees were taken from first principles of GC to the practical optimization of column selection and use.

V. New Solventless Sample Preparation Techniques: Janusz Pawliszyn, University of Waterloo, November 8, 2000.

Professor Pawliszyn is the leading pioneer of the technique of solid phase microextraction (SPME). In this seminar, he described basic principles relating to the use of SPME, and showed several examples of rapid, solventless analyses by using this technology. New developments were described to the 40 LSB and external staff who attended the seminar.

Publications, Presentations and Methods

Laboratory Services Branch

A. Publications

1. J. Carron, G. Kanert, J. Mills, D. Morse and D. Whitman. Evaluation of Headspace GC and Purge and Trap GC-MS for the Analysis of Volatiles in TCLP Leachates; *Proceedings of the Third Biennial International Conference on Monitoring and Measurement of the Environment 2000*, 285-290.
2. Patrick Crozier, J. Plomley and V. Taguchi. The Characterization of Nonylphenol Ethoxylates in Sewage Treatment Plants using Liquid Chromatography - Tandem Mass Spectrometry; *Proceedings of the Third Biennial International Conference on Monitoring and Measurement of the Environment 2000*, 53-60.
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B. Presentations

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2. M. Sage and V. Taguchi. Improvements to the Determination of Ambient Volatile Organic Compounds (VOCs) Using Thermal Desorption/Gas Chromatography-Mass Spectrometry (TD/GC-MS). Presented at the 48th ASMS Conference on Mass Spectrometry and Allied Topics, Long Beach, CA, June **2000**.
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8. *M. Pitcher*, *L. Nguyen*, *S. Lemanik*, *L. Matchuk* and *P. Yang*. Waterborne PAH Analysis Using Solid Phase Extraction (SPE), Toluene Microextraction and GC / MS Detection - A Critical Evaluation; Presented at the Third Biennial International Conference on Monitoring and Measurement of the Environment, Ottawa, May **2000**.
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12. *S. Selliah*, *S. Cussion*, *E.J. Reiner*, *K.A. MacPherson*, *T.M. Kolic*, *D. Toner* and *B. Chittim*. A Reference Material for Routine Performance Monitoring of Methods Measuring Dioxin-Like Compounds in Solid Matrices. Presented at the 20th International Symposium on Halogenated Environmental Organic Pollutants and POPs, Monterey CA, August 13-17, **2000**.
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15. *R.E. Clement*. The Importance of Science to Environmental Policy Making. Invited Seminar Presented to 4th Year Environmental Science Students, York University, October 23, **2000**.
16. *R.E. Clement*. Environmental Careers in Today's Workplace. Invited Seminar Presented to Environmental Program Students, Humber College, September 30, **2000**.
17. E.J. Reiner and *R.E. Clement*. The Challenges and Promise of Fast GC/MS. Presented at the 46th International Conference on Analytical Sciences and Spectroscopy, Winnipeg, Manitoba, August 15, **2000**.
18. *R.E. Clement*. Environmental Careers. Invited Seminar Presented to Environmental Technology Students for Career Day, Georgian College, July 19, **2000**.
19. *Lorna Grey*, Bick Nguyen and Paul Yang. Liquid Chromatography/Electrospray Isotopic Dilution Mass Spectrometry Analysis of Glyphosate in Environmental Samples. Presented at Joint Meeting of 32nd Eastern Canada Pesticide & Environmental Contaminants Workshop and the 19th Annual Meeting, Northeast Regional Section, AOAC International, Halifax NS., June **2000**.
20. *S. Selliah*, S. Cussion, K. MacPherson, E. Reiner and D. Toner. Development of a Reference Material (LSBRM9801) for Routine Performance Monitoring of Methods Measuring Polychlorinated Dibenzo-p-Dioxins, Polychlorinated Dibenzofurans and Dioxin-like Polychlorinated Biphenyls in Solid Matrices. Presented at the 8th International Symposium on Biological and Environmental Reference Materials, Bethesda, MD, USA, September **2000**.
21. *Eric Reiner*. Analysis of Persistent Organic Pollutants in Environmental Samples Using Microbore GC Columns. Presented at meeting *Accelerating Science*, Agilent Technologies, Mississauga, December 7, **2000**.
22. *Cammy Mack*. Laboratory On-Site Assessments – MOE Site Clean-up Guideline. Presented to MOE-Approvals Branch Staff and Ontario Private Laboratory Staff, MOE-Laboratory Services Branch, Etobicoke, January **2000**.
23. *Cammy Mack*. Analytical Data from Private Laboratories – Is There a Problem? Presented at MOE-Operations Division Biannual District Managers' Conference, Ryerson Polytechnical University, Toronto, February **2000**.

24. *Cammy Mack*. Laboratory Testing and Accreditation. Presented at 2000 Health Canada – Ontario Regional Environmental Conference, Niagara Falls, November 2000.
25. *Cammy Mack*. Reporting of Good Quality Laboratory Analytical Data – How Can We be Sure? Presented at 2000 Groundwater Monitoring Network Conference, Richmond Hill, Ontario, November 2000.
26. *Eric J. Reiner*. Analysis of Dioxin and Toxic Organics, Data Quality Objectives and Method Selection. Presented at University of Guelph, Department of Environmental Toxicology, Departmental Seminar, March, 2000.

C. New Laboratory Services Branch Analytical Methods

1. E3412: *The Determination of Polychlorinated Biphenyl Congeners (PCBs) in Soil, Sediment and Vegetation by Gas/Liquid chromatography-Electron Capture Detection (GLC-ECD)* [contact Robert Brunato]
2. E3414: *The Determination of Polychlorinated Biphenyls (PCBs) Congeners, Polycyclic Aromatic Hydrocarbons (PAHs), Chlorobenzenes (CB) and Organochlorines (OC) in Large Volume, Ambient Water Samples by Solid Phase Extraction (SPE) and GC-MS* [contact Stephanie Lemanik]
3. E3418: *The Determination of Polychlorinated Dibenzo-p-Dioxins, Polychlorinated Dibenzofurans and Dioxin-Like Polychlorinated Biphenyls (DLPCBs) in Environmental Matrices by Gas Chromatography–Mass Spectrometry (GC-MS)* [contact Eric Reiner]
3. E3420: *The Determination of Total Petroleum Hydrocarbons (C5 to C50) in Water and Effluents by Headspace Gas Chromatography-Flame Ionization Detection (GC-FID) Combined with Liquid/Liquid Extraction and GC-FID* [contact Dave Morse]
4. E3421: *The Determination of Petroleum Hydrocarbons in Water for the Decommissioning of Sites by Gas Chromatography-Flame Ionization Detection (GC-FID) and Gravimetry* [contact Dave Morse]

New Dorset Research Facility Analytical Methods - 2000

1. E3422: *The Determination of Molybdate Reactive Silicates and Dissolved Organic Carbon in Water and Precipitation by Colourimetry* [contact Don Evans]



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